

Spiral cracks in drying precipitates

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We investigate the formation of spiral crack patterns during the desiccation of thin layers of precipitates in contact with a substrate. This symmetry-breaking fracturing mode is found to arise naturally not from torsion forces, but from a propagating stress front induced by the fold-up of the fragments. We model their formation mechanism using a coarse-grain model for fragmentation and successfully reproduce the spiral cracks. Fittings of experimental and simulation data show that the spirals are logarithmic, corresponding to constant deviation from a circular crack path. Theoretical aspects of the logarithmic spirals are discussed. In particular we show that this occurs generally when the crack speed is proportional to the propagating speed of stress front.

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Fracture of solids produces a large variety of fascinating patterns. Straight and wiggling cracks in fragmented dried out fields, rocks, tectonic plates and paintings, and the self-affine fractured surfaces are just a few well studied examples. Understanding fracture and fragmentation phenomena is of increasing interest in physics and engineering [1]. Many recent studies have analyzed the morphology of fractured surfaces and fracture lines [2], most of which showing a cellular and hierarchical pattern. Concomitantly, successful models have been proposed to describe crack propagation and to reproduce the observed structures [3].

Apart from the cellular type, spiral, helical and in general smoothly curving fracturing modes are known in material science [4]. Most of the known spiral cracks are either due to imposed torsion (twist) as in the spiral fracture of the tibia [5], or due to geometric constraints as in the fracture of pipes [6]. Spiral cracks can, however, also arise in situations where no obvious twisting is applied, so that the symmetry is spontaneously broken. An example of this was recently given by Hull [7] in the study of the shrinkage of silica based sol-gel. Similar structures were reported by us for the post-fragmentation process of a thin layer of drying precipitate [8]. The formation of spiral cracks under specific conditions was also recently considered by Xia and Hutchinson [9]. In this letter, the mechanism leading to this special cracking mode shall be investigated and modeled. We shall discuss some mathematical properties in the shape of the spiral and reproduce them by computer simulations.

The experimental conditions leading to such structures are simple, one can do that without a laboratory. The first step is to produce by chemical reactions a fine suspension of precipitate. The spiral cracks are not restricted to one peculiar material, as we obtain them with different compounds, including nickel phosphate ($Ni_3(PO_4)_2$, from the reac-

tion between $NiSO_4$ and Na_3PO_4), ferric ferrocyanide ($Fe_4[Fe(CN)_6]_3$, from $K_4[Fe(CN)_6]$ and $FeCl_3$) and ferric hydroxide ($Fe(OH)_3$ from $FeCl_3$ and $NaOH$). The reacting salts are diluted in distilled water to concentrations between 0.3 – 10% for all reactions. Mixing the two reacting solutions produces the desired compound. The solution is then left to sediment and the dissolved ions (Na^+ , K^+ , Cl^- , SO_4^{2-} , ...) are removed by rinsing with distilled water. This gives us an aqueous suspension, which is then poured into a Petri-dish and let dry. During drying a thin solidified layer is formed which is then fragmented into isolated parts (Fig. 1a).

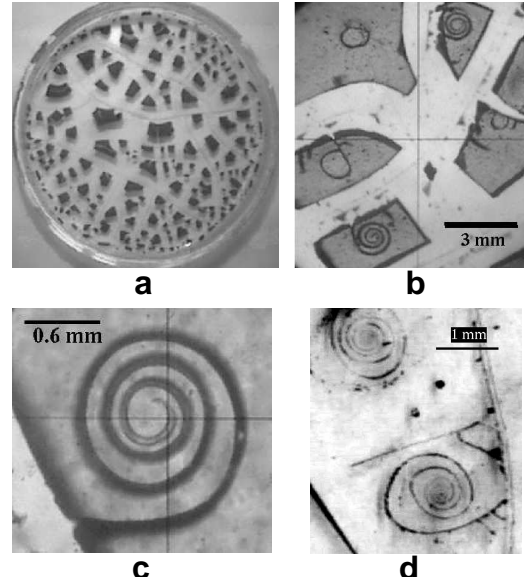


FIG. 1. Fracture of nickel phosphate precipitate at different length scales. (a) Typical fragmentation pattern inside a Petri-dish, (b) spiral and circular structures inside the fragments, (c) close-up of a spiral crack and (d) traces of the spiral cracks left on the glass surface.

For fine and thin precipitate (grain-size smaller than a few hundreds of nm and layer thickness between 0.2 to 0.5 mm), regular spirals as well as other smoothly curving cracks (such as circles, ellipses, and intersecting arcs) finally show up *inside* the fragments (Fig. 1b). Depending on the grain size and layer thickness the size of these fascinating structures varies widely, ranging from several hundred microns to about 5mm. Easily overlooked by naked eye, they are revealed under a microscope (Fig. 1c). Moreover, after removal of the layer, they leave beautiful marks on the glass surface (Fig. 1d).

By digitally analyzing their shape we found that all those spirals are approximately logarithmic, i.e., described by the functional form

$$r(\theta) = r_0 e^{k\theta}, \quad (1)$$

where r_0 and k are constants, with k determining the overall tightness of the spiral. r and θ are the polar coordinates in plane (in our convention θ can take any real value, not restricted to $[0, 2\pi]$). A characteristic fit is presented in Fig. 2, showing their logarithmic nature.

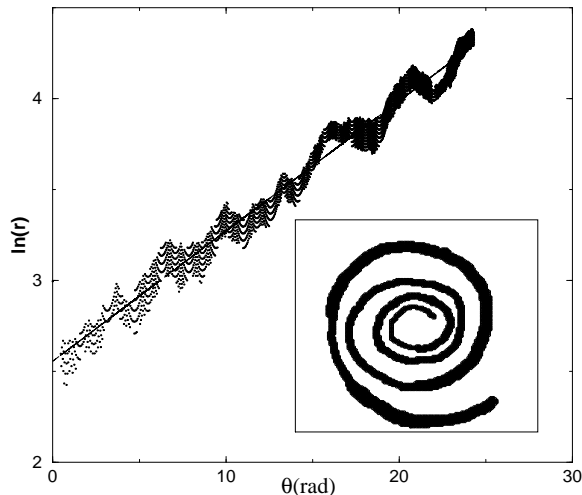


FIG. 2. A spiral crack in ferric ferrocyanide precipitate and a fit of its trajectory in polar coordinates. The linear fit has a slope of 0.072.

Read from the slope, the values of k from 14 instances of spirals are summarized below, for two different compounds and five different layer thickness. For ferric ferrocyanide we got: 0.075 (sample I.), 0.067 (sample I.), 0.080 (sample I.), 0.082 (sample I.), 0.086 (sample I.), 0.059 (sample II.), 0.072 (sample II.); for nickel phosphate: 0.078 (sample III.), 0.075 (sample III.), 0.063 (sample III.), 0.061 (sample III.), 0.061 (sample IV.), 0.078 (sample V.), 0.058 (Sample V.) Some observations can be made at this point:

(i) The logarithmic spiral, also known as the equiangular spirals, has been studied extensively since the 17th century by Descartes, Torricelli and Jacques Bernoulli. In addition to the well-known example in nautilus shells [10], it also describes the shapes of the arms of some spi-

ral galaxies such as NGC 6946 [11], and the flight path of a peregrine falcon to its prey [12].

(ii) The apparent length-scale r_0 from equation (1) can be absorbed in the phase: $r(\theta) = e^{k(\theta-\theta_0)}$, with $\theta_0 = -\ln(r_0)/k$. This demonstrates that the logarithmic spirals are scale-free.

(iii) Surprisingly, the majority of experimentally measured values of k fall between 0.06 and 0.08. The fluctuation among different spirals of the same sample is of the same magnitude as that among different samples with different compounds and thickness. This indicates a mechanism independent of layer thickness and precipitate type for the formation of the observed spiral cracks.

(iv) There are pronounced oscillations accompanying the linear trend in all our fittings, as exemplified in Fig. 2. These oscillations are almost periodical, and increases with r (note the logarithmic scale.)

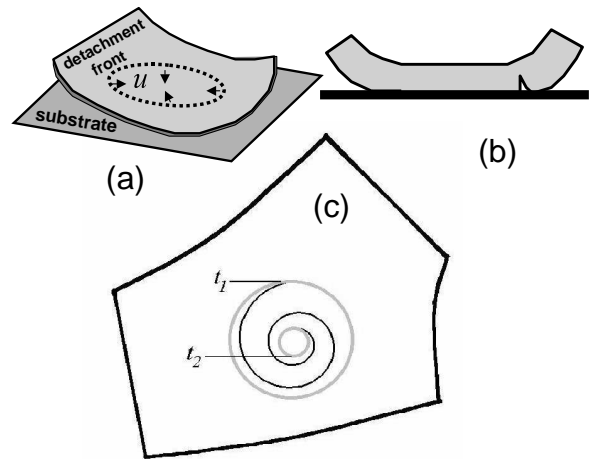


FIG. 3. The proposed mechanism for generating spiral cracks: (a) After primary fragmentation, a fragment folds up due to desiccation with a shrinking detachment front, (b) crack nucleation along the front and (c) the advancement of the front from time t_1 to t_2 leads to an inward propagating spiral crack.

In-situ observations under microscope during the desiccation process suggests the following mechanism. The spirals and circle-shaped structures are formed only after the primary fragmentation process is over. Due to the humidity gradient across the thickness, the fragments gradually fold up and detach from the substrate (Fig. 3a-3b), generating large tensile stress in the radial direction, at and normal to the front of detachment. The extend of the attached area shrinks as the ring-shaped front advances inward due to ongoing desiccation. When the stress at the front exceeds the local material strength, a crack is nucleated (Fig. 3c). Since the nucleation is seldom symmetrical with respect to the boundaries, the crack tends to propagate along the front in one preferred direction

where more stresses can be released. In the absence of further nucleation event, by the time the crack growth completes a cycle the front has already advanced, forcing the crack to turn further inward, resulting eventually in a spiral crack (Fig. 3d). Since the stresses on the top of the layer are mostly relieved by folding, they are concentrated at the layer-substrate interface. Therefore, the spiral runs like a tunnel, with 20 – 60% penetration into the layer thickness. The patterns being largely spiral means that crack propagation is favored over nucleation, for otherwise we would have observed more cylindrical concentric structures.

We now investigate in more detail the conditions under which the logarithmic spiral cracks can be produced. Denote the speed of the inward propagating drying front by u and the speed of the crack tip by v . We choose the origin as the center of the spiral. The trajectory of the crack is parameterized by the linear distance s , the radial distance r , and the polar angle θ , as shown in Fig. 4.

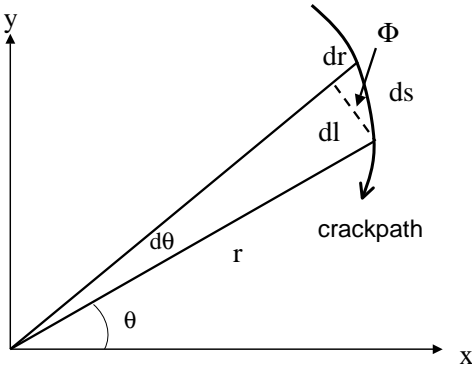


FIG. 4. Parametrization of the crack path.

For infinitesimal $d\theta$, we have $dl = r d\theta$, $(ds)^2 = (dr)^2 + (dl)^2$, and $\tan \Phi = dr/dl$. Then:

$$u^2 = \left(\frac{dr}{dt}\right)^2 = \left(\frac{dr}{d\theta}\right)^2 \left(\frac{d\theta}{dt}\right)^2, \quad (2)$$

$$v^2 = \left(\frac{ds}{dt}\right)^2 = \left[\left(\frac{dr}{d\theta}\right)^2 + r^2\right] \left(\frac{d\theta}{dt}\right)^2. \quad (3)$$

Eliminating $d\theta/dt$ from (2) and (3) we obtain:

$$\frac{dr}{d\theta} = \frac{ur}{\sqrt{v^2 - u^2}} = kr, \quad (4)$$

where

$$k \equiv \frac{u}{\sqrt{v^2 - u^2}} = \tan \Phi. \quad (5)$$

For constant k , we get (1), i.e., a logarithmic spiral. Physically, since $k(u, v)$ is a function of u/v alone, this result implies that the general condition for a logarithmic spiral to occur is to have a constant ratio between the two velocities, despite the possibility that the actual

dynamics may be very complicated and neither speed is constant. In other words, the logarithmic spiral structure is surprisingly robust to dynamical details. On the other hand since it is reasonable to expect a quasi-static crack to follow the direction of maximal stress relief, the geometric result of a constant angle Φ suggests that the orientation of the maximal stress component is constantly bending away from the instantaneous direction of propagation. The fact that all fitted values of k fall within a narrow range means that the degree of such bending is insensitive to details like the thickness or the chemical composition. More theoretically, one could ask if the Cotterell and Rice criterion [13] applies here: whether the stress intensity factor, K_{II} , vanishes along a constant inclination as the crack propagates under the influence of a radially symmetric stress field. If so, a logarithmic spiral is naturally expected.

Now we turn our attention to the oscillations that decorate the logarithmic behavior, as displayed in Fig. 2. Such oscillations indicate the departure from radial symmetry in the underlying stress field. It can be explained on the basis of boundary effects. Clearly the shape of a typical fragment is generally polygonal, not circular, and so its free boundaries will modify the shape of the shrinking stress front, more so the closer the front is to the boundaries. This leads to periodic variations in Φ , and hence oscillation in k . For rectangular fragments we expect to see two cycles of oscillation per revolution of the spiral. This is indeed roughly the case in our fits. Moreover, the observed diminishing amplitude of oscillation at smaller r is also in agreement.

To confirm and test the robustness of our proposed mechanism, we implement it in a mesoscopic spring-block model [14] which describes fracture of an overlayer on a frictional substrate. In this model, the grains in the layer are represented by blocks which form a triangular array of linear size L with interconnecting bundles each of which has H bonds (Hookean springs). The bond has a breaking strength F_c and a relaxed length l . While H plays the role of thickness, the initial block spacing a prescribes the residual strain $s = (a - l)/a$. Each block has the same slipping threshold F_s such that whenever the magnitude of the resultant force \vec{F} on a block exceeds F_s , the block slips to an equilibrium position defined by $\vec{F} = 0$. The temporally increasing stress in the layer during desiccation can be modeled by increasing the stiffness of the bonds. This is however equivalent to the case of constant stiffness but decreasing F_s and F_c , with fixed $\kappa \equiv F_c/F_s$. In this way, the competition between stick-and-slip and bond breaking, quantified by the set of parameters $\Gamma = \{s, \kappa, H, L\}$, was shown to give rise to realistic fragmentation and select the emerged scale [14].

Here we focus instead on what happens after the fragmentation process has settled. The simulated system is thus assumed to represent a fragment stable against the primary fragmentation (ensured by choosing Γ properly), but susceptible to secondary curved crackings induced by

an advancing stress front. Therefore, an inhomogeneous stress field is imposed, with a profile constant everywhere at σ_0 except on an annular region of radius R , where there is a hump of height $\Delta\sigma$ and width w (see upper inset of Fig. 5). By decreasing R at a constant speed u , we model the advancing front of stress field caused by detachment. In a rather narrow parameter region (mainly small u , large κ , $\Delta\sigma \sim \sigma_0$ and $w \approx a$), the desired spiral cracks are successfully reproduced (lower inset of Fig. 5). Consistent with experiment, the simulated spirals also follow a logarithmic form as illustrated in Fig. 5. The value of k depends on the parameters of the model. In particular, imposing smaller penetration results in tighter-binding spirals and hence smaller k . This is consistent with the screening effects of the existing crack on the stress field that influences further propagation of the crack.

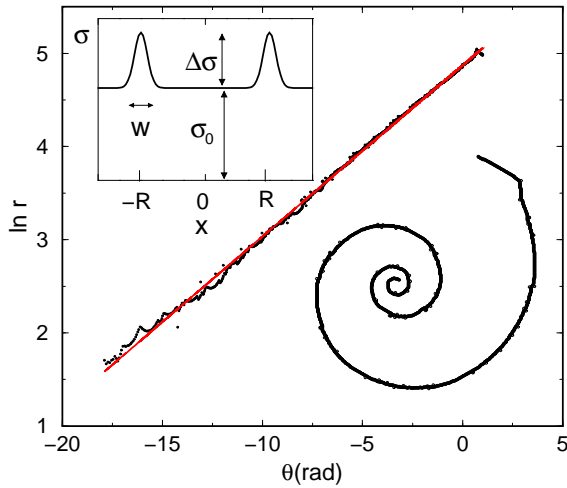


FIG. 5. A simulated spiral crack (lower inset) and a fit of its trajectory. The simulation parameters are: $L = 300$, $s = 0.3$, $\kappa = 2$, $H = 4$, $\Delta\sigma/\sigma_0 = 1.4$, $w = a$, speed $u = 0.005a/\text{step}$, and full penetration. The linear behavior indicates a logarithmic spiral, with a slope ≈ 0.184 . Upper inset: schematic plot of the stress profile imposed on the fragment.

In conclusion, spiral crack, an astonishing member of the family of fascinating patterns produced by fracture, is realized in a surprisingly simple setup of desiccating precipitate. Their formation is argued to be driven by an unusual stress relaxation process governed by the fold-up of the fragments. A discrete spring-block model incorporating such a driving appears to capture successfully the observed phenomena. The spirals have interesting properties, of which several quantitative aspects can be understood theoretically.

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